SUPERFUND SITE CLEANUP OF CHROMATE CONTAMINATED GROUNDWATER

By Dick Chmielewski, Published in Soil & Groundwater Magazine, December 1999/ January 2000

The Boomsnub site in the state of Washington was listed as a Superfund site in 1995. the site consists of two parcels of land, previously containing two unrelated businesses, which contributed separately to soil and groundwater contamination. The Boomsnub Metal Plating facility operated on about 0.5 acres, from 1967 to 1994. This facility was responsible for releases of chromium contaminated wastes which resulted in contaminated soil and groundwater by hexivalent chrome.

Across the street from the Boomsnub site, on approximately four acres, is an active compressed gas production facility. Various organic releases at this location have resulted in volatile organic compounds (VOCs) contamination of both soil and groundwater. Migration of the groundwater has resulted in a merged plume containing both chromium and VOCs. Both locations have been combined as one site for purposes of environmental investigation and remediation.

For the chrome contamination, ion exchange was selected as the cleanup technology. A standard weak base anion resin was selected to remove the dissolved hexivalent chromate, which is an anion. The state installed an anion exchange system in 1992 to handle groundwater contaminated by chromate. Also at this time, the building housing the plating business was demolished and removed from the site along with 6,000 tons of contaminated soil.

Under normal range of pH (1-10), and at low concentrations, chromium is present in groundwater as either monovalent, HCr_2O_7 , or divalent chromate, CrO_4 . The monovalent form predominates in acidic water while the divalent form predominates at neutral pH and above. At the Boomsnub site, divalent chromate is the major species present.

$2 \text{ R OH} + \text{CrO}_4^{-2} \text{R}_2 \text{CrO4} + 2 \text{ OH}^-$	(1)
$R_2CrO_4 + 2 NaOH \rightarrow 2 R OH + 2 Na^+ + rO_4^{-2}$	(2)

The initial ion exchange process for chromate removal used a macroporous tertiary amine weak base anion resin. This system, sized to treat the 50 gpm flow rate, while effective, was found to be costly to operate due to limited resin capacity and expensive regeneration. Equations 1 and 2 show the ion-exchange and regeneration reactions for the chromate ion – WBA resin system.

As can be seen by equation 1, which represents the service cycle, the resin readily removes chromate from the contaminated ground water. This requires two exchange sites for each chromate ion. A weak base anion resin was selected for its relatively high capacity and reasonable selectivity for chromate.

Equation 2 represents the regeneration cycle in which the hydroxyl ion deprotonates the amine to form water, releasing the chromate from the resin as a sodium salt.

One concern with regenerating ion exchange resins in this type of application is that the spent regeneration solution contains high concentrations of the heavy metals, in this case chromium.

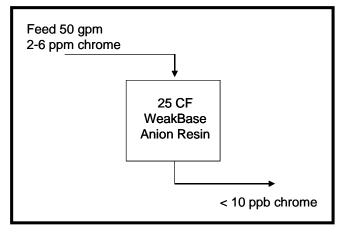
Care must be taken to handle and dispose of this waste stream in an environmentally acceptable way. Commercial regeneration facilities licensed to regenerate such resin are available, but the price for such service is expensive as can be seen below in the economic evaluation.

The initial Weak Base (WB) anion exchange system consisted of a single vessel containing 25°CF of resin and was operated at a flow rate of 50 gpm as shown in Figure 1. Typical feed concentrations for chrome were 2-6 ppm as chrome. The maximum contaminant limit (MCL) for chrome in drinking water has been established by the EPA as 100 ppb. The loading obtained with this system was about 2 lb Cr/CF of resin. This corresponded to a treated volume of 2.5 Million gallons. Regeneration frequency was therefore on the order of 30 - 40 days.

Chrome Selective Resin

The initial 50 gpm system was operated for about two years, when it was proposed that a specialty, chromium selective resin be evaluated for this project. The chrome slective resin is a specialty anion resin with a proprietary functional group, which is very selective for chromate. The capacity of the specialty resin for chromate is more than three times that of the standard weak base anion resin. This means that the instead of having a capacity of 2.5 million gallons to exhaustion, the same volume of the chrome selective resin can treat approximately 7.5 million gallons before capacity is achieved.

Run lengths are increased from 30 - 40 days to more than 90 days. Although the chrome selective resin is more expensive than a standard weak base anion resin, the significantly higher capacity allows the system to operate in a one-time use or throwaway mode. That is, the resin is used once and



disposed of along with soil removed from the site, to a secured, approved landfill for hazardous waste. Figure 1. Initial 50 gpm system

This avoids the expense of regenerating a resin containing a heavy metal such as chrome. The cost to perform this regeneration are high since the chrome-rich stream produced in the regeneration needs to be treated in an environmentally acceptable way. The chrome is bound to the solid resin beads and cannot be leached out with water, thereby immobilizing the chrome when placed in a secured landfill.

As can be seen from Table 1, the economics shows that the one-use operation of the chrome selective resin is about 15 % less than using a standard weak base anion resin with regeneration. Also note that the capacity of the standard weak base anion resin is too low to consider one time use. It would be about 50 % more expensive to use the standard weak base resin on a one time use basis than to regenerate this resin.

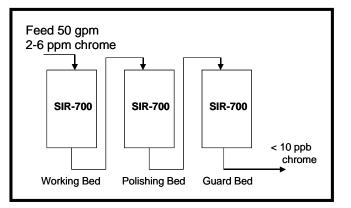
The chrome selective resin was recommended and initial testing was very encouraging. On the basis of these tests a new larger system was designed and built.

Three Bed System

A new three-bed system was designed to treat a flow rate of 100 gpm, as shown in Figure 2. Each bed contains 50°CF of chrome selective resin. The three-bed system, which was built in 1994, operates as follows: The first bed is the working bed. This bed does the initial removal of chromate. The effluent quality from the first bed is monitored and when the bed is no longer removing chrome, it is removed from service.

The second bed is the polishing bed. This bed begins to remove chrome when the first bed becomes exhausted.

The third bed is the guard bed. When the first bed



is removed from service, the second bed becomes

the working bed and the guard bed becomes the polisher.

Figure 2. three bed system

After removing the resin from the first bed and installing new resin, it is returned to service as the new guard bed.

In this way the beds and the resin are cycled through the plant to achieve extremely high capacity for chrome removal. This system has been in successful operation for five years. The system is very effective in removing chrome from the contaminated groundwater. The treated water from this system is discharged to the City of Vancouver POTW.

<u>Future Plans</u>

In August of 1999, the EPA issued a proposed plan to upgrade the existing treatment system. The EPA evaluated seven alternatives for improving the cleanup of the Boomsnub site. The preferred and recommended alternative is to continue to use the ion-exchange technology with the highly selective chrome resin and to increase the treatment capacity of the system to 200 gpm. This proposal will involve drilling more wells to remove contaminated groundwater at a faster rate to insure that the contaminant plume does not spread beyond the existing boundaries and to improve treatment in areas of highest concentration.

The treatment system can be easily upgraded by installing three new tanks and the associated piping. The two systems with three tanks each can be operated in parallel. It is anticipated that this system will be installed within a year.

Specialty ion exchange resins for removal of heavy metals has shown to be an economical treatment technique for control of chromate contamination at the Boomsnub Superfund site. This technology would be equally effective for other heavy metals including mercury, nickel and lead. Specialty resins are also available for nitrate and several other specific contaminants.

	Standard WB-	Standard WB – Throw –	Specialty Resin Throw – away
	Regenerated	away	
Resin Cost	\$780.	\$37,500.	\$22,500.
Regen Cost	\$22,500.	-	-
Labor Cost	3,840.	\$ 3,840.	\$ 1,280.
Total Cost	\$27,120.	\$41,340.	\$23,780.
Notes: 1. Standard WB resin cost based on 4 year life. 3. Labor costs based on 16 man-hours to unload and load 25 CF tank. 2. Regeneration cost based on \$75/CF for chrome-laden resin. 4. Throw-away standard WB changed out 12 times per year.			

Throw-away specialty resin changed out 4 times per year.

